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Phenoxy-mercapto Derivatives of Group 4 Alkoxides as Core-Shell precursors to Group 4 Ceramic-Coinage Metal Nanomaterials.

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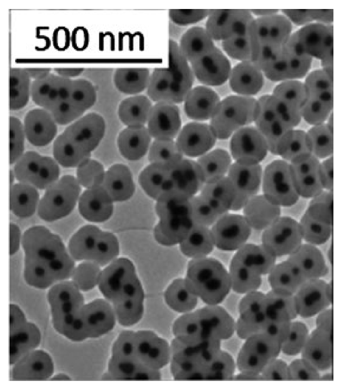
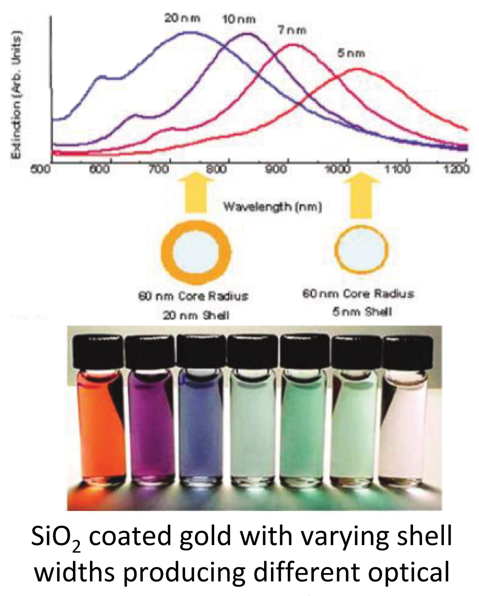
Core-shell nanoparticles have a wide variety of applications

Nanoparticles can be broken down into two categories based on their make-up. Simple nanoparticles are made from a single material while composite or core-shell nanoparticles are composed of two or more different materials. While there are many ways to form a heterogeneously composed particle, the simplest is concentric spherical core-shell construction.



TEM of typical spherical core-shell nanoparticles[2].



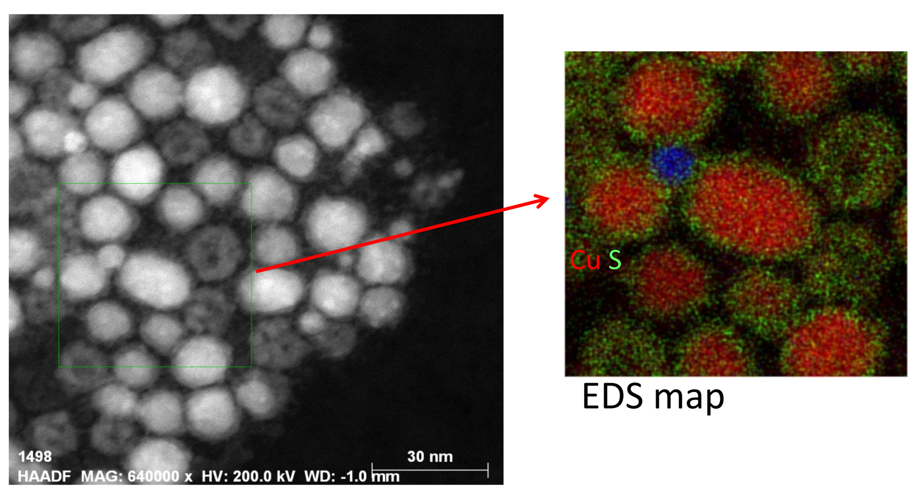
SiO_2 coated gold with varying shell widths producing different optical resonances[1].

Core-shell nanomaterials have attracted interest based on their potential to demonstrate modified properties from the individual component's characteristics. The shell feature offers many advantages to the core such as increasing: stability, solubility, biocompatability, controlled release/access. TheTiO_2 on gold system is of interest for many applications such as fuel cells, photovoltaic devices, and catalysis[1,2].

1. Chaudhuri, Rajib; Paria, Santanu. "Core/Shell Nanoparticles: Classes, properties, Synthsis Mechnisms, Characterization, and Applications" *Chemical Reviews* **2012** *112*, p22373-2433.
2. Lekeufack, D.D.; Miele, P. "Core-shell Au@(TiO_2,SiO_2) nanoparticles with tunable morphology" *Chem Comm.,* **2010,** 46, 4544-4546.

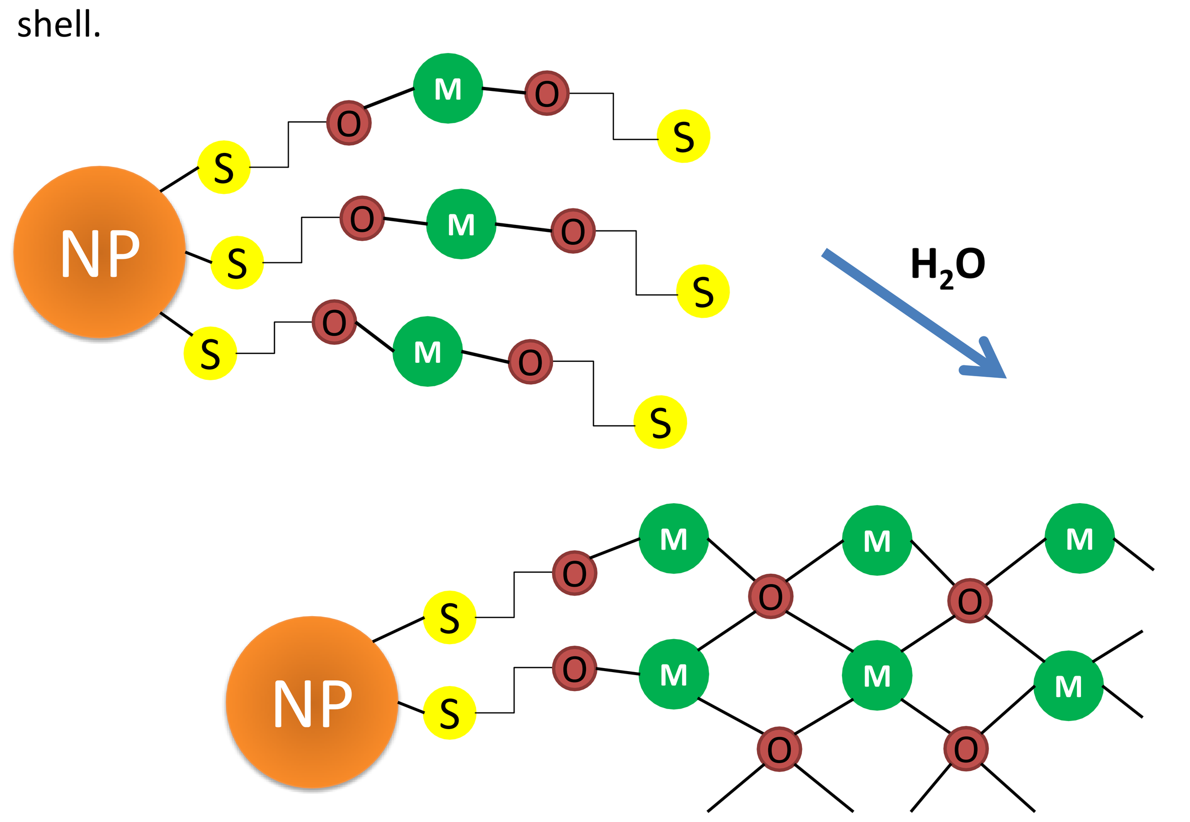
Can exploiting the thiol-coinage metal interaction introduce additional control the ceramic shell coating?

Thiols have long been used to cap nanoparticles and prevent further aggregation. Long chain thiols like dodecanethiol are the most popular method for capping gold nanoparticles because of their near covalent bond-strength to the noble metal[3].



TEM of Cu nanoparticles, exposed to thiol containing atmosphere. Sulfur readily reacted with the Cu to form CuS/Cu core-shell nanoparticles.

Copper and silver nanoparticles also have a high affinity for sulfur. Thiol ligands, along with amine ligands, are also very popular as capping agents for Ag/Cu nanoparticles. For coinage metal cores (i.e., Cu, Ag, Au), the coating of the metal with ceramic oxides by soft chemistry methods is limited, with most of the reports detailing the hydrolysis and heating of an added metal halide to form the ceramic shell.

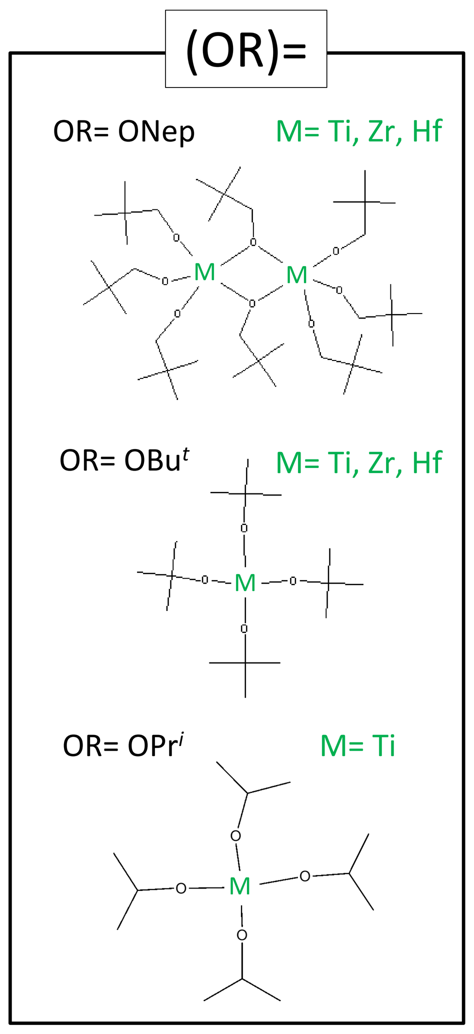


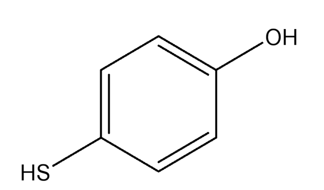
In this experiment we propose using this soft chemistry approach to bind a functionalized metal alkoxide to the nanoparticle surface in situ. Then, through hydrolysis, form a ceramic oxide shell

3. Krishnendu Saha; Rotello, Vincent M. "Gold nanoparticles in Chemical and Biological Sensing" *Chemical Reviews* **2012** *112*, p2739-2779.

Novel group 4 metal alkoxide-thiols were synthesized for investigation as capping agents

$$M(OR)_4 + n\,(H\text{-}4MP) \xrightarrow{Tol/\,py} [M(OR)_{4-n}\,(4MP)_n] + n\,H\text{-}OR$$

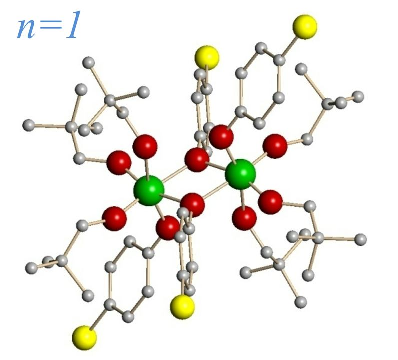




4-Mercaptophenol (4MP)

To a stirring solution of the appropriate $[M(OR)_4]$ in the desired solvent (tol or py), *n* equivalents of H-4MP ligand were added. The mixture was stirred for a minimum of 12 h and then set aside with the cap loose until crystals formed. If a precipitate formed, the sample was heated until the precipitate dissolved and then set aside until crystals formed.

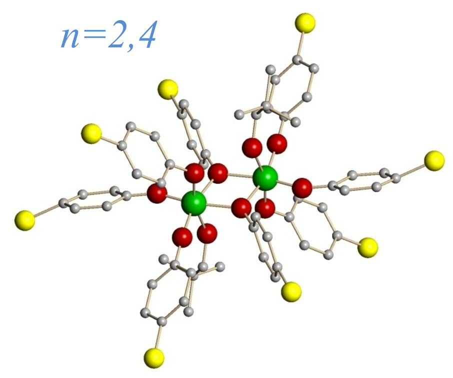
n=1



$M_2\,(u\text{-}4MP)_2(4MP)_2(ONep)_6$

1:1 reaction yields crystalline tetra-substitued dimers as the product across all OR groups and metals

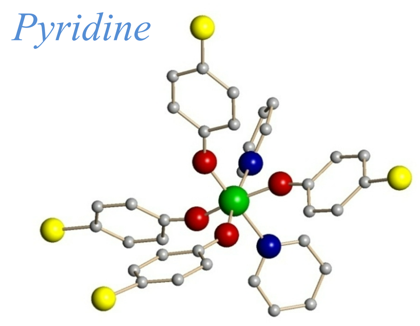
n=2,4



$M_2\,(u\text{-}4MP)_2(4MP)_6(ONep)_2$

1:2, 1:4 reactions yield crystalline fully substituted dimers with a protonated HOR group left coordinating to the metal. The product is similar across all OR groups and metals

Pyridine

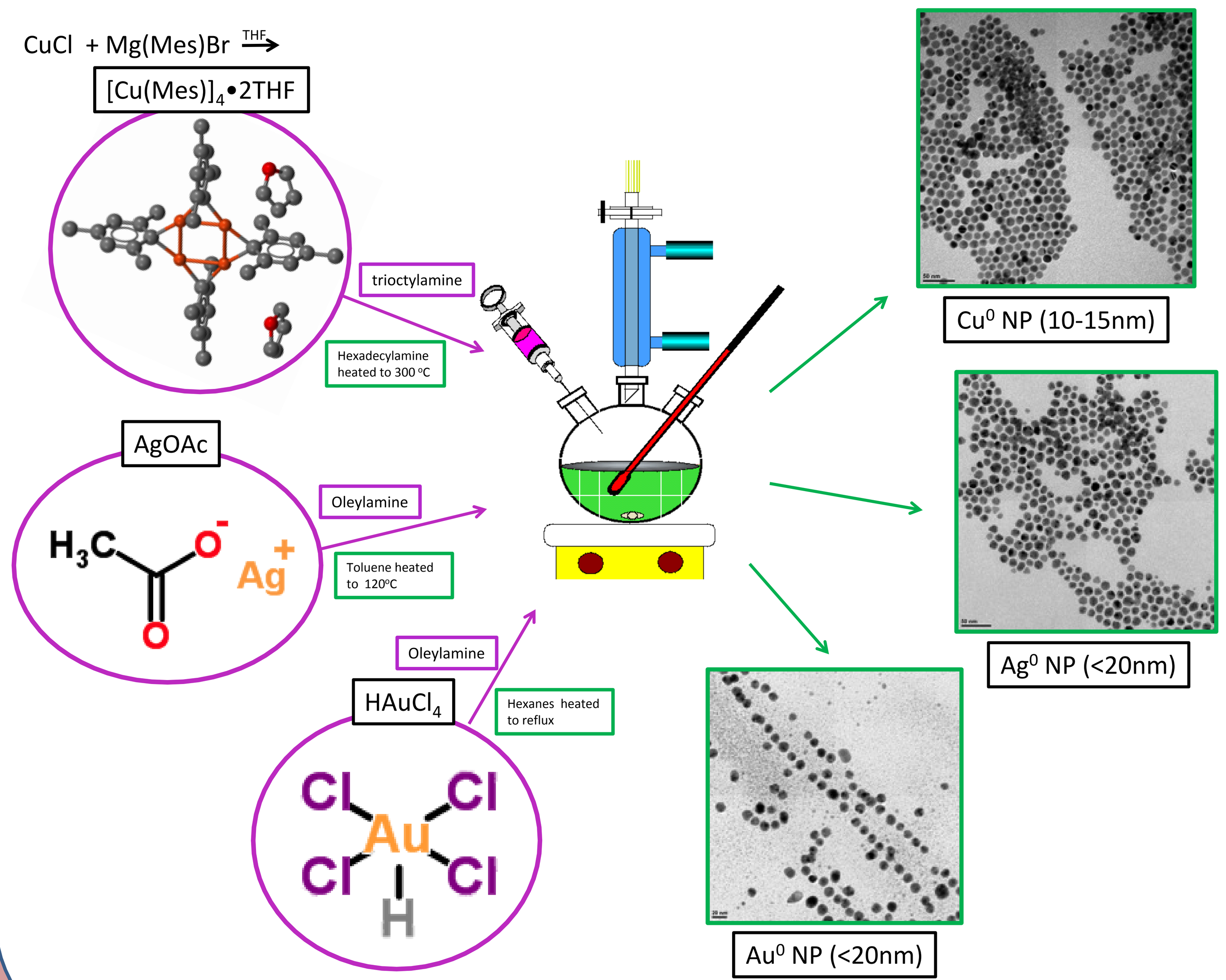


$M(4MP)_4(py)_2$

When run in pyridine, all reactions yield a crystalline monomeric species with four covalently bound 4MP ligands and two coordinating solvent molecules

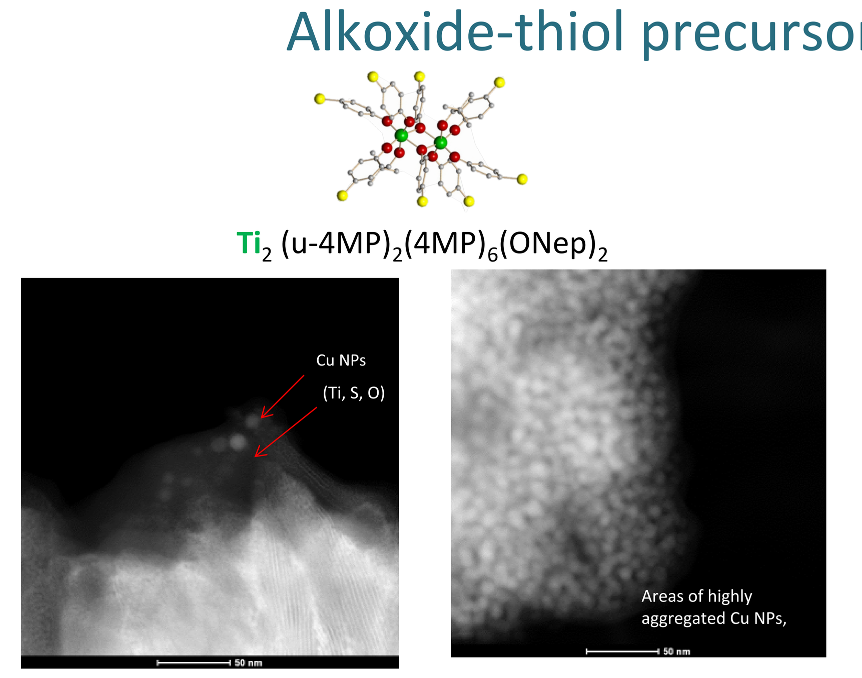
Au, Ag, and Cu nanoparticles were synthesized using solution precipitation methods

A solvothermal (SOLVO) route was taken to synthesizing each nanomaterial precursor. In these routes, nanoparticles (NP) are generated by the La Mer growth process and grow by Ostwald ripening. As a supersaturated solution exceeds the nucleation threshold and reaches the critical limiting super saturation point, a homogeneous 'nucleation shower' occurs resulting in the formation of growth nuclei. After this, the precursor concentration drops below the nucleation threshold, resulting in no new particle formation. With progression of time, particles grow based on Ostwald ripening. The Cu[4,5], Ag[3], and Au[3] (NP) synthesis are described below.



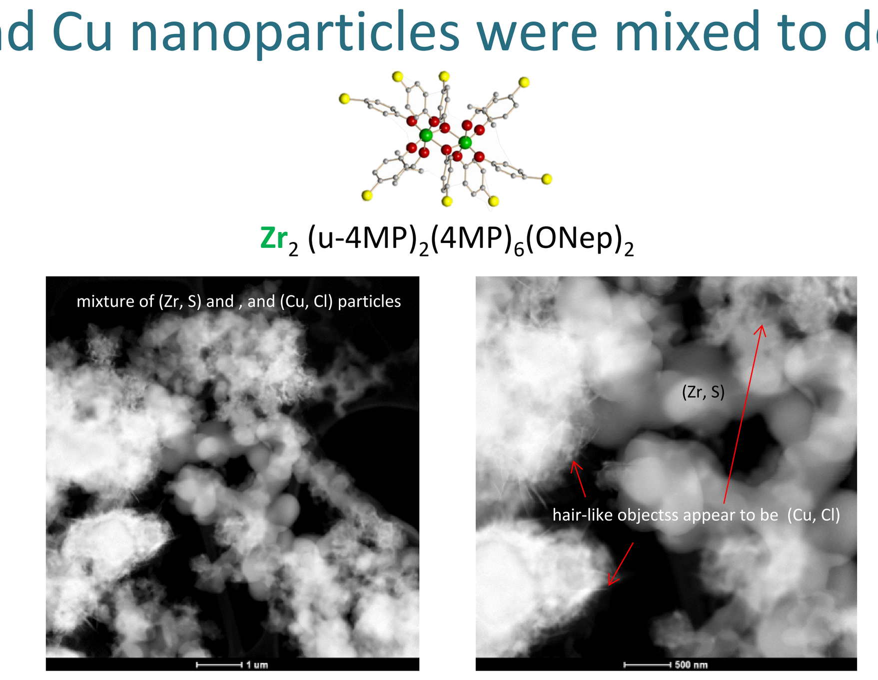
4. Bunge, Boyle, Headly "Synthesis of Coinage-Metal Nanoparticles from Mesityl Precursors" *Nano Letters* **2003** *3*, 901.
5. Scott D. Bunge and Timothy J. Boyle, "Synthesis of Metal Nanoparticles" (USA), 2005

Alkoxide-thiol precursor and Cu nanoparticles were mixed to determine initial interactions



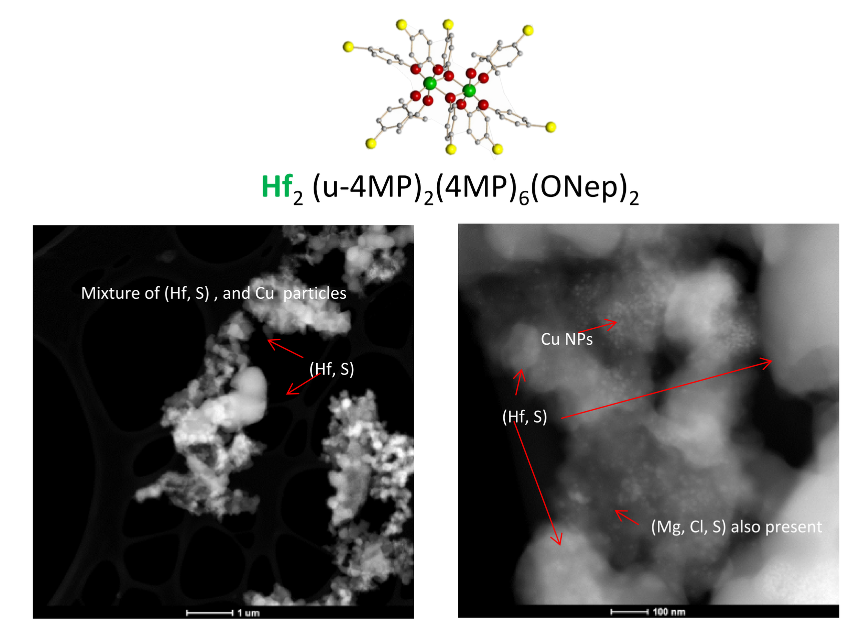
TEM images Ti(4MP) and Cu mixture. Chemical make up determined with EDS.

Upon mixing, the titanium alkoxide appears to be interacting with the Cu NPs. However, the interaction is limited and there are many groups of unperterbed, aggregated NPs. This is unexpected due to the free 4MP ligand available in solution. It's possible a layer of oxide is protecting the samples.



TEM images Zr(4MP) and Cu mixture. Chemical make up determined with EDS.

The Zr(4MP)/Cu mixture has a unique contaminant revealed in the TEM image. $CuCl_{1-2}$ hair-like structures are abundant on the grid. This could be a remnant of the Cu(Mes)2 reaction however, the product is filtered and no $CuCl_2$ was seen in the TEM of the other mixtures or in the PXRD of the Cu NPs.



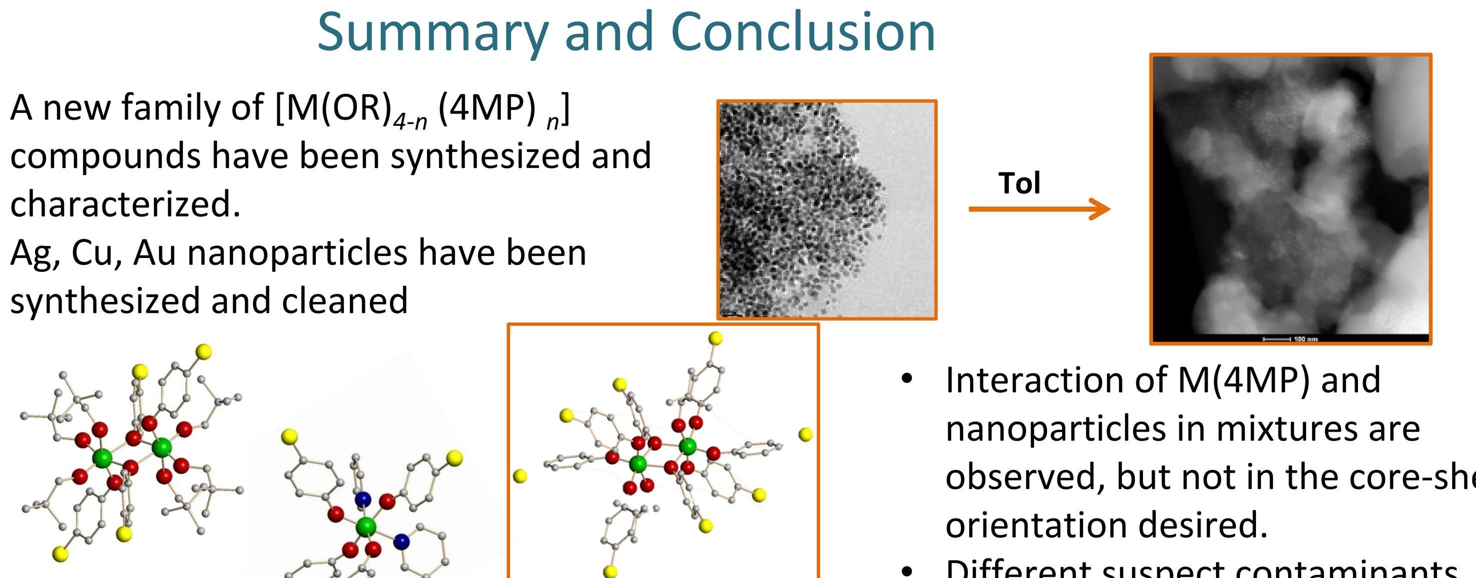
TEM images Hf(4MP) and Cu mixture. Chemical make up determined with EDS.

The Hf(4MP)/Cu mixture has similar interactions to the Ti4MP/Cu mixture. The Hf4MP appears to be coating large aggregates (~150nm clumps) of CuNPs. Another strange contaminant is present, $MgCl_2$. This could also be attributed to the $Cu(Mes)_2$ but it is not seen in the other mixtures.

Note: Due to instrument outages, the samples were left on the grid for a month before testing. More samples have been prepared and prompt testing is expected.

Summary and Conclusion

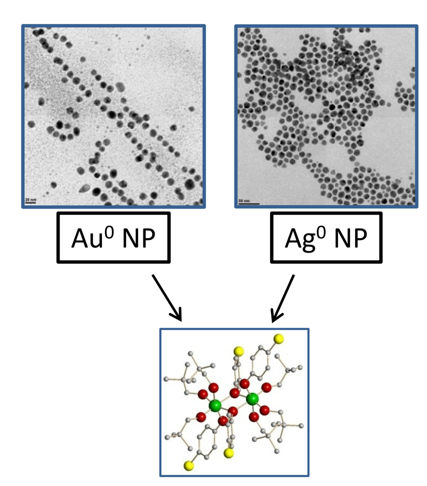
- A new family of $[M(OR)_{4-n}\,(4MP)_n]$ compounds have been synthesized and characterized.
- Ag, Cu, Au nanoparticles have been synthesized and cleaned



- Interaction of M(4MP) and nanoparticles in mixtures are observed, but not in the core-shell orientation desired.
- Different suspect contaminants were seen. Solutions have been remade and submitted for TEM analysis.

Future Work

- Run the rest of the nanoparticle series (Ag, Au) with the different 4MP alkoxides to see if interactions differ from
- Evaluate fresh sample results to determine validity of suspect contaminants.
- Mix less substituted alkoxides with the nanomaterials to determine if the substitution has an effect on the interaction.



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